PHOTOCHEMICAL METHODS IN CHEMICAL ANALYSIS

1. Literature review

By

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Recent development in the field of analytical photochemistry is reviewed and systematized. The essential characteristics of methods such as photonometry, photocatalytical method, photogravimetry, end point detection by photochemical indicator reaction, methods based on photodissociation, etc. are elucidated by typical examples.

To date photochemical reactions have found little application in chemical analysis. Until twenty years ago, to the best of our knowledge there was only a single method based on a photochemical reaction [1]. In contrast, a number of references drawing attention to the negative role of photochemical reactions could be found: the photosensitivity of many substances (their fading or change in colour) leads to a positive or negative error in their determination, and to poor reproducibility of the measurements.

Research during the past twenty years has produced an increasing number of data proving that photochemical reactions can be more than simply a source of error; they can also provide new possibilities for chemical analysis. This is not surprising if it is remembered that photochemical reactions have a number of favourable features not possessed by ordinary chemical reactions. For example, the nature of the reagent in photochemical reactions, the photon, can readily be changed by variation of the wavelength of the light used for irradiation, and by this means the selectivity of a reaction can be increased. The rate of a photochemical reaction can be influenced by regulating the intensity of the photon current. Another advantage is that addition of the reagent can be completed by stopping the irradiation; in this way one may avoid the reagent excess which arises in traditional analysis and which may bring about further transformation of the reaction product. A further substantial advantage results from the fact that photochemical reactions are in general fairly sensitive and accordingly permit the determination of microcomponents, too.

Since these advantages of photochemical reactions have been increasingly utilized in recent years, we considered it timely to compile a brief review of the results attained in this developing field of analysis, in spite of the fact that two monographs were published not too long ago [2, 3]. One of these was not written from a purely analytical aspect, and accordingly it does not present all the principles of measurement. The other monograph is definitely analytical in outlook, and gives a faithful picture

of the relevant results up to roughly the end of 1972. This monograph has the added value that it also deals with those photochemical reactions which the authors consider might possibly be used as basis for future analytical procedures. Even though these monographs have appeared, we consider publication of our review to be justified, for our conceptions differ from those of the authors mentioned as regards the analytical evaluation and the classification of the photochemical reactions employed.

From the aspect of chemical analysis the procedures based on photochemical reactions can be classified in the following way.

1. Photonometry, photochemical production of the reagent

The essence of this method is that the reagent is produced in a solution of the substance to be determined, by irradiation of a suitable auxiliary reagent with light of constant intensity; the reagent produced then reacts instantaneously with the substance to be measured. According to the Bunsen—Roscoe law, the amount of substance formed in a photochemical reaction is proportional to the product of the light intensity and the duration of the irradiation, and thus the amount of the substance to be determined can be obtained by measuring the duration of the irradiation. This can be done in several ways. One possibility is to observe the appearance of the product of the photochemical reaction. This can be followed directly if this substance is coloured, while if it is not, or not sufficiently, coloured, then it is converted to a coloured substance with a suitable reagent and observed in this way. If the substance to be determined is coloured, the end-point of the photochemical titration can be established by measuring the decrease in its absorption. Naturally, not only optical, but other end-point indicating methods, too, may be possible. It is clear that this method is analogous to the indirect, or reagent-developing coulometric method. This principle was employed by YOKOYAMA and IKEDA [4] in the following way for the determination of thallium(III). A uranium(VI) salt and lactic acid were added to the thallium(III) solution to be analized, the solution was irradiated with light of constant intensity, and the appearance of the uranium(IV) band was observed spectrophotometrically. When irradiated, uranium(VI) is reduced by lactic acid to uranium(IV), which in turn reduces thallium(III). The end-point of the reaction is indicated by the appearance of a uranium(IV) excess.

BRICKER and SCHONBERG [5] determined chromate and vanadate by irradiating these compounds in the presence of iron(III) and oxalic acid. The iron(II) formed in the photolysis of iron(III)+oxalate reduces chromate to chromium(III), and vanadate to vanadium(IV). The increases in the amounts of chromium(III) and vanadium(IV) were followed spectrophotometrically.

SMITH and FITZGERALD [6] used the tungsten(V) formed on the photolysis of tungsten(VI) and glucose for the titration of vanadate, chromate and ferricyanide. The end of the titration was indicated by the appearance of the blue colour of the tungsten(V). The above determinations were performed with the aid of calibration curves (amount of substance *vs.* time).

2. *Photocatalytic procedures*

The procedures listed under this heading can be carried out in two ways. In one possibility a reaction which is slow under normal conditions is made to take place at a rate suitable for analytical measurements by adding a photocatalyst (photon-carrier, sensitizer) to the solution and irradiating the system.

With appropriate selection of the experimental conditions, a possibility arises for the determination of the amount of the photocatalyst. Irradiation is performed with light of constant intensity for a definite period, and the extent of the transformation of the substance used for the measurement is determined; this is proportional to the amount of the photocatalyst.

With the aim of the determination of chromium(VI), ALMÁSSY *et al.* [7, 8] accelerated the slow reaction between chromate and methyl orange by irradiating with ultraviolet light. This was achieved by adding an iron(III)-oxalate photon-carrier system to the solution under examination. In this case the chromate can be titrated directly with a methyl orange solution. In addition to the direct determination of chromium(VI), this procedure was also applied for the indirect measurement of the iron(II) ion and hydrogen peroxide. In the latter two cases chromate was added in excess, and the excess was titrated with methyl orange solution.

SIERRA *et al.* [9, 10] employed photocatalysis to accelerate the reactions between peroxydisulphate and iron(II) or mercury(I). The peroxydisulphate was titrated with iron(II) solution during irradiation, in the presence of erythrosin-B as photon-carrier, together with silver and iodide ions. Erythrosin-B dye was employed as photocatalyst on titration with mercury(I) solution. A 160 watt tungsten lamp was used as light source.

The other possibility of photocatalysis was discovered by KHARLAMOV, MANTSEVICH and DODIN [11], who made use of the iron(III)-catalyzed photooxidation of organic dyes for the determination of iron(III). It was stated that when the organic matter—metal ion system is subjected to light, electron-transfer occurs from the organic substance to the metal ion acceptor. If the solution also contains oxygen, then under suitably selected conditions the oxygen assumes the role of the electron-acceptor, while the metal ion becomes a catalyst. Under favourable concentration conditions the relation between the extent of decolouration of the dye and the metal ion concentration is linear. The method was employed to determine the iron contents of nickel and cobalt.

For the determination of micro amounts of uranium, NEMODRUK and BEZROGOVA [12] added ethanol and methylene blue to a solution containing uranium(VI), and irradiated the system. If oxygen is excluded, the uranium(IV) formed in the photoreduction reduces the methylene blue to the colourless leuco compound, which in the process is reoxidized to uranium(VI). This is again reduced to uranium(IV), which reduces a further molecule of methylene blue, and so on. Thus, the loss of colour of the dye in a definite time is proportional to the uranium(VI) concentration.

The microdetermination of uranium can also be performed in ethanolic medium in the presence of oxygen. The primary products in the photoreduction are then uranium(IV) and acetaldehyde. In the presence of oxygen, however, peroxide derivatives, too, are produced in the course of the irradiation, and these oxidize uranium(IV) to uranium(VI). This is capable of oxidizing a further alcohol molecule to aldehyde,

and so on. Thus, measurement of the aldehyde concentration provides a sensitive method for the determination of uranium [13].

Although the mechanism of the photochemical reactions taking place in the oxalic acid+uranyl ion system is by no means clarified as yet, it can nevertheless be effectively used for analytical purposes. The reaction can be characterized as the uranyl ion-sensitized photodecomposition of oxalic acid:

$$H_2C_2O_4 \xrightarrow[h\nu]{UO_2^{2+}} H_2O + CO_2 + CO$$

According to PEIGE *et al.* [14], under suitable conditions the rate of consumption of oxalic acid is a function of the uranyl ion concentration. The excess of oxalic acid can be determined by permanganate titration. TAYLOR *et al.* [15] employed the above reaction for the determination of uranium by measuring the pressure of the gaseous products.

3. Application of photochemical indicator reactions

In certain cases the reaction between the titrant solution and the photocatalyst can be utilized to indicate the end-point of a titration. SIERRA *et al.* [16] used the reaction between EDTA and dyes of thiazine type as an indicator reaction. It has long been known that thionine or methylene blue in oxygen-free solution oxidizes EDTA if the system is illuminated. This is somewhat surprising, for EDTA is fairly resistant to even the stronger inorganic oxidants. The leuco dye can be measured voltametrically on a Pt anode. This can be utilized to indicate the end-point in the titration of certain metal ions (*e.g.* lead(II), copper(II), magnesium(II), etc.) with EDTA. During the titration the solution is illuminated with a tungsten lamp, and the formation of the leuco form is observed with the aid of anodically polarized rotating Pt and saturated calomel electrodes. Originally only a residual current is observed, as no free EDTA is present in the solution. However, when the equivalence point is exceeded, the excess EDTA reduces the thionine and the anode current commences. The amperometric end-point can readily be detected. The method is fairly slow, as it is necessary to wait at least 2 minutes after each addition of titrant solution for a well-perceivable current effect to develop.

4. Photogravimetric methods

In these procedures the component to be determined is subjected to a photochemical reaction either directly or *via* a suitable developing reagent; by this means the substance is converted to a precipitate of well-defined composition, the weight of which is measured after the customary operations.

SINGH and PATNAIK [17] solved the determination of uranium(VI) in the presence of iron(III) and vanadium(V) by prolonged irradiation of the solution in question, after addition of ethanol and ammonium fluoride. In the presence of ethanol, uranium(VI) is transformed to uranium(IV), which reacts with the fluoride to give a

poorly-soluble precipitate of composition $NH_4F \cdot UF_4 \cdot H_2O$. This conception was used, too, for the separation of uranium from beryllium and zirconium [18].

With the aim of the precipitation of uranium, DIENERT and VILLEMAINE [19], as well as SPITZIN [20] irradiated a uranyl nitrate solution in the presence of hypophosphite. On irradiation the hypophosphite reduces the uranium(VI) and immediately reacts with the uranium(IV) produced to give a precipitate, $U(H_2PO_2)_4$.

For the gravimetric determination of mercury(II) SAKURABA and IKEYA [21—23] irradiated the solution in question in the presence of manganese(II) oxalate in hydrochloric acid medium, and weighed the mercury(I) chloride thus precipitated.

5. Indirect photochemical analytical methods

Photochemical reactions provide fairly extensive possibilities for chemical analysis if the photolysis is used to bring the component to be determined into a measurable form. The substance is subjected to exhaustive photolysis ("reagent" excess) directly or in the presence of an appropriate photon-carrier, and the product is determined (directly or indirectly).

RAO *et al.* [24] demonstrated that uranium(VI) undergoes reduction on the action of light in the presence not only of ethanol, but also of other primary and secondary alcohols; tertiary alcohols, however, exhibit weaker effects. The uranium(IV) formed was titrated with sodium vanadate.

RAO and SANTOPPA [25] used formaldehyde as reductant and similarly titrated the uranium(IV) produced with sodium vanadate, in the presence of N-phenylanthranilic acid or diphenylbenzidine as indicator.

NEMODRUK and BEZROGOVA made a detailed study of the photochemical reduction of uranium(VI) in the presence of ethanol in media of sulphuric acid [26] and phosphoric acid [27]. They examined the effects exerted on the photoreduction by the duration of the irradiation, the temperature, the sulphuric acid or phosphoric acid concentration and the amount of ethanol. The uranium(IV) resulting from the reaction was determined by titration with ammonium vanadate. If the phosphoric acid concentration of the starting mixture was higher than 2.5 M, more ammonium vanadate was consumed than the amount corresponding to the uranium(VI) content. In our view, this is due to the circumstance that at higher phosphoric acid concentrations in the presence of oxygen the ethanol gives rise not only to acetaldehyde, but also to peroxy derivatives, and these latter consume vanadate. This assumption is supported by the fact that a product which can be titrated with ammonium vanadate is obtained even if an acetaldehyde solution is subjected to prolonged irradiation in the absence of uranium [28].

The microdetermination of uranium can be carried out only in oxygen-free medium if the uranium(IV) produced by photoreduction in 0.5—1.0 N sulphuric acid is determined with arsenazo(III). In the presence of oxygen the measurements are subject to a negative error, for the uranium(IV) is partially reoxidized to uranium(VI). The finding that, in contrast with the micro method, the macrodetermination of uranium does give an acceptable result in the presence of oxygen [29] can be explained by the fact that the vanadate solution does not only react selectively with the uranium(IV); it rather gives a measure of the overall reducing capacity of the mixture. The uranium(IV) deficiency in the acid concentration range 1.2—2.5 M

is compensated by the equivalent amount of peroxy compounds formed by oxidation with oxygen, for these peroxy compounds also consume vanadate.

The photochemical reduction of molybdenum(VI) was studied by TANANAEV and LOKHVITSKAYA [30]. Their work served as a basis of a determination of molybdenum by PRASAD and SURYANARAYANA [31]. Molybdenum(VI), in its photoreduction with thiocyanate ion in hydrochloric acid medium, is transformed to molybdenum(V). The molybdenum(V) reacts with the thiocyanate excess to form a stable, coloured complex, which is suitable for the spectrophotometric determination of molybdenum.

KHARLAMOV and KOROBOVA [32] carried out the photoreduction of molybdenum(VI) in the presence of tartaric acid, and similarly measured the molybdenum(V) in the form of its thiocyanate complex. They assumed that on irradiation an excited tartaric acid molecule is formed; a hydrogen atom can then easily split off and give rise to the reduction. We consider it more probable that the photolysis of the molybdenum tartarate complex, which is fairly stable in the pH range 2—5 [33, 34] leads to the photoreduction of the molybdenum(VI). This assumption is supported by the finding that the photoreduction of molybdenum(VI) is complete in the pH range 1—6, while from pH 7 to pH 8 the efficiency of the photoreduction decreases rapidly. NEMODRUK and BEZROGOVA [35] employed ethanol for the photoreduction of molybdenum(VI). The photoreduction was faster in oxygen-free medium than in the presence of oxygen (the molybdenum(V) formed is very stable on standing in air). The molybdenum(V) was determined in the form of its thiocyanate complex.

The photoreduction of rhenium(VII) was investigated by the above authors in media of hydrochloric acid [36] and sulphuric acid [37]. In the presence of ethanol in hydrochloric acid solution, with the exclusion of oxygen, ultraviolet light causes rhenium(VII) to be reduced first to rhenium(V), and then to rhenium(IV) (rhenium(IV) and rhenium(V) are sensitive to the oxygen of the air!). The absorption of the rhenium(IV) itself was used for its spectrophotometric determination. In sulphuric acid medium thiourea was employed as reductant and the rhenium(IV) formed was determined spectrophotometrically in the form of its thiourea complex.

The photoreduction of neptunium(VI) and the possibility of its quantitative determination in this way were investigated by NEMODRUK and BEZROGOVA in perchloric acid [38] and hydrochloric acid [39]. It was found that irradiation of neptunium(VI) and neptunium(V) in the presence of ethanol (with suitably chosen experimental parameters) results in rapid and quantitative reduction to neptunium(IV). The neptunium(IV) was measured spectrophotometrically in the form of its complex with arsenazo(III). Formic acid, too, appeared suitable for the photoreduction of neptunium(VI) in the presence of ethanol.

The contradicting views in the literature with regard to the photochemical reduction of tungsten(VI) were clarified by NEMODRUK and BEZROGOVA [40]. In the presence of ethanol, tungsten(VI) undergoes quantitative photochemical reduction to tungsten(V) if 4 M phosphoric acid is applied for the acidification. The tungsten(V) can be determined spectrophotometrically in the form of its thiocyanate complex, or by titration with ammonium vanadate.

Numerous organic substances are suitable for the photochemical reduction of iron(III). RAO *et al.* [41, 42] studied the photoreduction of iron(III) in the presence of oxalic, lactic, citric and amygdalic acids, and NOVÁK [43] also used oxalic acid. The iron(II) formed was determined by titration with sodium vanadate, with di-

phenylbenzidine or diphenylsulphonic acid as indicator, or spectrophotometrically, in the form of its complex with *o*-phenathroline. NOVÁK and AREND [44] carried out the determination of iron(III) traces in sodium citrate and sodium tartrate by immediate irradiation of solutions of these materials in the presence of *o*-phenanthroline, with measurement of the intensity of the colour of the resulting iron(II) complex.

RAO and ARAVAMUDAN made use of the photosensitivities of the iron(III)-oxalate [45] and the cerium(IV)-oxalate [46] systems for the quantitative determination of oxalic acid. In the case of the former system iron(II) is formed in an amount equivalent to the oxalate and was determined with sodium vanadate. In the cerium(IV)-oxalate system the excess of cerium(IV) after irradiation was determined by titration with iron(II).

RAO and RAMACHARLU [47, 48] utilized the photoreaction of mercury(II) chloride with sodium oxalate for the volumetric determination of mercury. The photoreduction of mercury(II) in the presence of the oxalate ion is very slow. The application of uranyl nitrate or iron(III) chloride as a photosensitizer leads to the photoreduction proceeding more rapidly, and the mercury(I) chloride can be measured iodometrically.

It is known that the yellow heteropolyacids of silicic acid and phosphoric acid with molybdic acid can be reduced with tin(II) chloride or sodium sulphite to silico- or phosphomolybdenum blues. The absorptions of these latter can be used to determine even microgramme quantities of silicon and phosphorus. The chemical reduction has the disadvantage that the reduced heteropolyacids are not stable, their absorptions varying with time. If the reduction is carried out photochemically, then the "blue compound" formed on irradiation exhibits an extinction decrease of only 3% in 24 hours. This can presumably be attributed to the fact that on the cessation of the irradiation the reductant disappears from the solution. NEMODRUK and BEZROGOVA [49] used tartaric acid and formic acid for the photoreductions of silicomolybdic acid and phosphomolybdic acid, respectively. The reduction was performed in 2N sulphuric acid, at which acid concentration it was found that the molybdic acid itself was not reduced [32]. The spectra of solutions of silicomolybdenum blue and phosphomolybdenum blue obtained by chemical reduction with tin(II) chloride and by photoreduction coincide, with a maximum at 800 nm.

ALIMARIN *et al.* [50] used the above findings as the basis of the determination of arsenic in the form of molybdenum arsenate. Formaldehyde was employed as reagent for the photoreduction, and the arsenomolybdenum blue produced was measured spectrophotometrically at 825 nm.

Another determination which can be included here is that of the nitrate ion. When methyl orange is subjected to ultraviolet irradiation in the presence of nitrate, the colour fades strongly. This reaction was utilized by DODIN *et al.* [51] for the determination of nitrate in the presence of other oxyanions.

6. *Procedure based on photochemical dissociation*

Such a procedure is suitable for the determination of compounds which undergo photochemical decomposition to yield a product measurable with satisfactory accuracy. This possibility was employed by DAIBER and PREUSMANN [52] to deter-

mine N-nitroso compounds, amines and amides. On photolysis, these compounds give rise to an equivalent amount of nitrite, which can be measure spectrophotometrically by means of the Griess—Ilosvay reagent.

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ФОТОХИМИЧЕСКИЕ МЕТОДЫ В ХИМИЧЕСКОМ АНАЛИЗЕ
1. Литературный обзор

А. Петер, Л. Й. Чани

В работе рассматривается современное развитие аналитических методов, основанных на фотохимических реакциях. На некоторых примерах рассмотрены свойства таких важнейших методов, как фотонометрии, фотокаталитического метода, фотогравиметрии, применения фотохимических реакций для обозначения конечных точек титрования и метода, основанного на фотодиссоциации.